

Coppola, Vito A.

Attorney Docket No. P04988US1

REMARKS**OVERVIEW**

Claims 22-37 are pending in this application. Claims 22, 28-32, 34 and 36 have been amended. The present response is an earnest effort to place all claims in proper form for immediate allowance. Reconsideration and passage to issuance are respectfully requested.

ISSUES REGARDING DOUBLE PATENTING

The Examiner has provisionally rejected claims 22-37 under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-17 of co-pending Application No. 10/047,709.

Only claims 6, 7 and 9 remain from co-pending and commonly owned Application No. 10/047,709. These 3 claims correspond to claims 28, 29 and 31 of the pending application. Claims 28, 29, 30 (a claim dependent on claim 28) and 31 are cancelled from the present application. It is respectfully submitted that the provisional double patenting rejection should be withdrawn.

ISSUES UNDER 35 U.S.C. § 103

Claims 22-27 and 32-37 are rejected under 35 U.S.C. § 103 as unpatentable over JP 04041676. A copy of a machine translation of JP 04041676 is enclosed. Claims 26 and 27 are cancelled making the rejections of these claims moot. Claims 22-37 are rejected under 35 U.S.C. § 103 as unpatentable over GB 2242203. Claims 26-31 are cancelled making the rejections of these claims moot.

JP 04041676 REFERENCE

Responding to the Examiner's arguments that JP04041676 discloses a Ni/Pt alloy heated at 500°C to 900°C in a reducing atmosphere, the Applicant respectfully consults the translation

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(enclosed) rather than just the English translation of the abstract. It should be noted that the Ni/Pt alloy in JP04041676 is 90/10 Pt/Ni resinate (see Embodiment 6(9)) while the current invention includes mixtures 10/90 Pt/Ni or even lower Pt concentrations, which is a clear advantage given the respective costs of such materials. Also, the heating of the alloy under a reducing atmosphere in JP04041676 is performed at temperatures between 500°C to 900°C while the current invention includes heat treatments in a reducing atmosphere at a higher temperature range, 1000°C or even 1100°C to the melting point of Ni. The difference in temperature ranges is significant. The clear advantage, superior oxidation resistance, of the higher temperature heated samples is shown in Fig. 1. Compare the oxidation resistance of the samples heated at 1300°C and the sample heated at 1000°C to the sample heated at only 500°C. Therefore the product-by-process limitations result in an alloy having different properties (such as the oxidation resistance) than what is disclosed in JP 04041676. Therefore, it is respectfully submitted that the rejections to claim 22 should be withdrawn. As claims 23-25 depend from claim 22, the rejections should also be withdrawn from these claims.

GB 2242203 REFERENCE

GB 2242203 discloses Pt/Ni compositions heated from 600°C to 1000°C in a reducing atmosphere. With respect to Examiner's assertion that GB 2242203 teaches that time and temperature profiles can be altered to achieve particular alloy characteristics, making the invention obvious, the Applicant respectfully submits that GB 2242203 teaches away from the present invention by teaching that temperatures above 1000°C are to be avoided. GB 2242203A states that:

"It is preferred to avoid temperatures significantly above 1000°C if the material is heated for any significant time, since sintering and loss of surface area may occur." (p. 8, lines 17-19).

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Therefore, GB 2242203 teaches away from the invention.

Motivation is lacking when the state of the art at the time of invention suggests a different direction than the one in which the inventor proceeded. In re Hedges, 228 USPQ 685, 687.

Further, claim 22 is amended to include the language "between 1100°C to the melting point of Ni" which is significantly above 1000°C. Therefore, this rejection to claim 22 should be withdrawn on that basis.

It appears that GB 2242203 teaches Pt loadings greater than 5 wt. % Pt, preferably 7.5 wt. % to 15 wt. %. In the same paragraph, above the 5 wt. % language, the reference notes that the preferred atomic ratio of platinum to the alloying elements (Ni) is 50:50. This corresponds to an alloy 76.9 wt. % Pt and 23.1 wt. % Ni. Therefore, it is difficult to say what GB 2242203 actually teaches.

No fees or extensions of time are believed to be due in connection with this amendment; however, consider this a request for any extension inadvertently omitted, and charge any additional fees to Deposit Account No. 26-0084.

Reconsideration and allowance is respectfully requested.

Respectfully submitted,

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(54) Title of the Invention: Formation method for a thin metallic film used on heat-resistant substrate

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Specifications:

1. Title of the Invention: Formation method for a thin metallic film used on heat-resistant substrate
2. Scope of the claims of the patent:

A Formation method for a thin metallic film to be used on heat-resistant substrate that is characterized by: Applying a mixture of a metallic resinate and an organic solvent onto the above mentioned metallic substrate, and after drying it is baked in an atmosphere of 300~400 Degrees Celsius. And next, further baked in an atmosphere of a reductive gas, or an inert gas containing a reductive gas at 500~900 degrees Celsius. This takes place within the formation method of a thin metal or a metallic alloy film having anti-oxidation properties to be used on substrate material.

3. Detailed description of the invention:

(Field of application in industry)

This invention relates to a formation method for thin metallic film that is used as industrial, and especially heat-resistant material on useful metallic substrates such as tungsten and molybdenum.

(Prior art, and the corresponding problem)

Although heat resistant materials excelling in high-heat strength such as tungsten and molybdenum are being utilized in resistor devices and heating elements, when utilized in high temperature / high oxidation atmospheres oxidation takes place and problems occur. Not just the degeneration of the functionality of the above noted resistor devices and heating elements, but fissures and disconnection can be caused in cases where the heat-resistant materials are used in thin-board or line form. Because of this, precious metals are being used as material in atmospheres having high oxidation and high temperature. But, because of the high cost of these precious metals mentioned, various kinds of composite materials are being utilized.

To rival the method of using plates of precious metals that excel in heat-resistance, methods such as sputtering methods, evaporation methods, electroplating methods, and pasting methods exist as formation methods for the thin film layers. As far as methods for forming the thin film (below 1u) the sputtering methods, evaporation methods, and electroplating methods are carried out, but because the equipment for the sputtering and evaporation methods are very expensive, it is undesirable for use in industrial mass production. With the electroplating method, application of plating to detailed areas is difficult, and the adhesion is lacking. Also, for the sake of freely choosing the right metal to convey the electricity, the varieties of plating liquid are lacking in number. Because of these reasons, there are many tasks that are in need of development.

(Purpose of the invention)

This invention was made to rectify the weak points of the above-mentioned "former methods". This invention provides a method for the formation of thin metallic film, as heat resistant material excelling in high temperature strength for the sake of improving the anti-oxidation properties on substrate materials such as tungsten and molybdenum, which are used in resistor devices and heating elements.

(Means for solving the problems)

This invention is a method for the formation of thin metallic film to be used on heat resistant substrate, it is characterized by: applying a mixture of a metallic resinate and an organic solvent to the above mentioned metallic substrate, and after drying it is baked in an atmosphere of 300~400 Degrees Celsius. And next, further baked in an atmosphere of a reductive gas, or an inert gas containing a reductive gas at 500~900 degrees Celsius. This takes place within the formation method of a thin metallic or a metallic alloy film having anti-oxidation properties to be used on substrate material. A description concerning the details of this invention will be carried out.

The formation method for a thin metallic or a metallic alloy film having anti-oxidation properties utilizes metallic resinate selected from such metals as platinum, gold, silver, palladium, rhodium, iridium, ruthenium, copper, and nickel, as it utilizes precious metals having superior anti-oxidation abilities as base metal. The above-mentioned metallic resinates must be changed to a metal by undergoing heat-decomposition at below 350 degrees Celsius.

The use of marketed products is acceptable as long as they are metallic resinates that are heat-decomposed at below 350 degrees Celsius as mentioned above. A solution had by combining and neutralizing an organic acid with either ammonia or triethylamine is added slowly under agitation, to a solution of a certain percentage of a metallic chloride or nitrate solution. This forms an oily resinate. Next, the oily resinate is extracted into chloroform and washed in water. After this, evaporation is carried out, and a metallic resinate is attained.

The above-mentioned organic acid utilized is selected from one of the following: Neopentanoate, Neoheptanoate, Neononanoate, Neodecanoate, N-heptanoate, or Ethylhexanoic Acid. Also, as long as it is the metallic resonate attained as mentioned above, the benefits are not just that a metal is attained by

heat-decomposition at under 350 degrees Celsius, but it is all the more desirable because of the fact that any impurities that can be detrimental to the thin film produced are removed. Terpineol is fine for use as the organic solvent. It is possible to change the amount of solvent added, in light of the thickness and application of the thin film to be formed. However, a film with a thickness of 0.1~0.5 μm can be attained by a single application, drying, and baking. It is easiest to attain a uniform thin film by using a percentage of metallic resinate of 5~30%.

It is possible to choose from a number of application methods for applying the mixture of the adjusted metallic resinate and the organic solvent mentioned above, to the surface of the heat resistant substrate. These application methods include, the paintbrush-application method, the screen-print method, the stamp method, the spray method, the dipping method, and the spin coating method. A suitable method is chosen in light of the shape and form of the substrate to receive the film, and the application style (i.e. application in part only, or full body application).

After the above-mentioned application stage, drying takes place at room temperature for approximately 10 minutes. After this drying stage, baking takes place at 350 degrees Celsius for approximately 10 minutes. Next, in an atmosphere of a reductive gas such as hydrogen, it is heated at 500~900 degrees Celsius for approximately 10 minutes for complete and thorough transformation into metal. Doing this will produce the desired thin metallic film having anti-oxidation properties and excellent adhesion strength to the surface of the substrate.

Although embodiments concerning this invention will be mentioned below, this invention is not limited to these embodiments.

Embodiment 1

A neutralized solution of ethylhexanoic acid and triethylamine is made to react with a solution of platinum IV potassium chloride at 40 degrees Celsius, and then extracted into chloroform. After this, it is washed in water and then evaporation is allowed to take place. A platinum resinate is the result. Next, a 7% solution of Terpineol is added to this platinum resinate to form a mixture. This mixture is applied to the surface of a tungsten substrate board (25.4mm x 25.4mm x 1.2mm (thickness)) using the screen-print application method, and allowed to dry at room temperature (20 degrees Celsius) for 10 minutes. Next, it is baked at 350 degrees Celsius for 10 minutes. After this, in an atmosphere of hydrogen it is heated to 700 degrees Celsius for 10 minutes in an electric furnace. The result is a uniform thin platinum film that has a thickness of 0.5 μm that has been formed on the surface of the tungsten board.

The same resulting thin platinum film formed on the surface of the tungsten board has been tested for adhesive strength using the dipping adhesion method as well. It has been confirmed that no peeling has taken place in correspondence to use of the dipping application method.

Also, when tested in an atmosphere heated to 1000 degrees Celsius for 30 minutes, surfaces of the tungsten board that were coated with the thin platinum film did not undergo oxidation, while surfaces that did not have the thin platinum film coating did undergo oxidation.

Embodiment 2

This embodiment was operated in the same manner as in embodiment 1, except that in this embodiment molybdenum board (25.4mm x 25.4mm x 1.2mm (thickness)) is used instead of a tungsten substrate board. The same thin Platinum film was formed in this embodiment as in embodiment 1, and the corresponding results attained in this embodiment are also the same as the results attained in embodiment 1.

Embodiment 3

Neutralizing Neodecanoate with either ammonia or triethylamine produces a solution. Either one of the following metallic chlorides or nitrates are reacted to the above mentioned solution: Gold potassium chloride solution, Gold trichloride solution, Silver nitrate solution, Palladium potassium chloride solution, palladium chloride solution, Rhodium potassium chloride solution, Rhodium nitrate solution, Rhodium chloride solution, Iridium potassium chloride solution, Iridium chloride solution, Ruthenium potassium chloride solution, ruthenium chloride solution, copper nitrate solution, copper chloride solution, nickel nitrate solution, nickel chloride solution. Next, it is extracted into chloroform. It is then washed in water and evaporation is allowed to take place. Finally, Gold resinate, Silver resinate, Palladium resinate, Rhodium resinate, iridium resinate, Ruthenium resinate, Copper resinate, or Nickel resinate are attained respectively.

A heat analysis has been carried out for the respective metallic resins that were attained above. The results measured of the heat-decomposition temperature for each metallic resinate have been displayed on the chart below.

Chart 1

Metallic Resinate	Heat Decomposition Temperature (°C)
Gold	2 1 0
Silver	2 4 0
Palladium	2 4 5
Rhodium	2 5 0
Iridium	2 8 5
Ruthenium	2 4 0
Copper	2 3 0
Nickel	2 1 5

Also, Terpeneol, Methanol, Dibutylcarbitol are used as organic acids and combined with the above-mentioned metallic resins to form their respective uniform solutions.

Embodiment 4

The Gold, Silver, and Copper resins of embodiment 3 are combined at a weight ratio of 92:5:3. A 10% solution of Terpeneol is then added and combined to this resinate. This mixture is applied to the surface of a tungsten substrate board with the screen-print application method, and then dried at room temperature (20 degrees Celsius) for 10 minutes. After drying, it is baked in an atmosphere of 350 degrees Celsius for a further 10 minutes. Then, in an atmosphere of hydrogen gas (Containing nitrogen gas 50%) it is heated to 600 degrees Celsius for 10 minutes in an electric furnace. The result is a uniform thin Gold, Silver and Copper combination film that has a thickness of 0.5um that has been formed on the surface of the tungsten board. The same resulting thin Gold, Silver and Copper

combination film formed on the surface of the tungsten board has been tested for adhesive strength using the taping adhesion method as well. It has been confirmed that no peeling has taken place in correspondence to use of the taping application method. Also, when tested in an atmosphere heated to 600 degrees Celsius for 30 minutes, surfaces of the tungsten board that were coated with the thin Gold, Silver and Copper combination film did not undergo oxidation, while surfaces that did not have the thin Gold, Silver and Copper combination film coating did undergo oxidation.

Embodiment 5

This embodiment was operated in the same manner as in embodiment 4, except that in this embodiment molybdenum board (25.4mm x 25.4mm x 1.2mm (thickness)) is used instead of a tungsten substrate board. The same thin Gold, Silver and Copper combination film was formed in this embodiment as in embodiment 4, and the corresponding results attained in this embodiment are also the same as the results attained in embodiment 4.

Embodiment 6

In this embodiment the metallic resins are used in the proportions shown below, and are applied, dried, baked in the same manner as in embodiment 1. The results attained are the same as the results attained in embodiment 1. Also, the results of the adhesive strength test, as well as the oxidation resistance test were the same as in embodiment 2.

[Types of metallic resinate, and the proportions of]

- (1) Platinum resinate 90%: Rhodium resinate 10%
- (2) Platinum resinate 85%: Gold resinate 15%
- (3) Platinum resinate 90%: Palladium resinate 10%
- (4) Platinum resinate 90%: Iridium resinate 10%
- (5) Platinum resinate 85%: Palladium resinate 10%: Ruthenium resinate 5%
- (6) Gold resinate 90%: Nickel 10%
- (7) Gold resinate 90%: Palladium resinate 10%
- (8) Platinum resinate 85%: Palladium resinate 10%: Copper resinate 5%
- (9) Platinum resinate 90%: Nickel resinate 10%

Chart 2

No	Adhesion Strength	Oxidation Test Results
①	No peeling	1 0 0 0 °C No Change
②	No peeling	1 0 0 0 °C No Change
③	No peeling	1 0 0 0 °C No Change
④	No peeling	1 0 0 0 °C No Change
⑤	No peeling	1 0 0 0 °C No Change
⑥	No peeling	0 0 0 0 °C No Change
⑦	No peeling	1 0 0 0 °C No Change
⑧	No peeling	0 0 0 0 °C No Change
⑨	No peeling	1 0 0 0 °C No Change

Embodiment 7

In this embodiment thin Platinum film is formed in the same manner as in embodiment 1. Application of the Platinum resinate, drying, baking, formation of the thin Platinum film is carried out in the same manner as in embodiment 1. The only difference is that instead of a plain tungsten substrate board, an aluminum board (25.4mm x 25.4mm x 1.2mm (thickness)) with a 1.0um thick tungsten film formed on the top surface of it was used. The adhesion strength tests, and oxidation resistance tests where the sample is heated at 900 degrees Celsius for 30 minutes, were also carried out. The adhesion strength is great, and the results of the oxidation resistance test were no different.

The effects of the invention

This invention utilizes precious metals and metal alloys as base metal for the metallic resinate. As shown in the results above these precious metals clearly possess anti-oxidation properties. The metal resinate is utilized, and with a small amount of organic solvent it is applied to the surface of a metallic substrate lacking in oxidation-resistance, and then dried and baked. With this extremely easy and convenient process it is possible to produce a thin film that excels in anti-oxidation properties. This provides a way to fully protect from oxidation the relatively easily oxidizing metals tungsten and molybdenum that come from the former methods of just being placed in a high temperature reductive gas atmosphere. And it is an invention that greatly contributes to the improvement of the development and reliability of the technology.